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CHARACTERISTICS OF FLUID FLOW IN THE COMBUSTION SYNTHESIS OF TIC FROM THE ELEMENTS*

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ABSTRACT

Finite reservoir effects on capillary spreading at small reservoir dimensions are explored numerically and related to wave propagation in combustion synthesis of TiC from elemental Ti and C. In addition a convective instability which may be activated by gravitational, surface tension or contact forces may cause void regions to coalesce thereby altering the void distribution in combustion synthesis products.

INTRODUCTION

The field of combustion synthesis of ceramics and alloys is now an old one [1] and it has long been recognized that in at least some systems the reaction generates fluid intermediates [2-7]. Yet little direct experimentation [4-7] or theoretical analysis [8,9] has been performed to understand the nature of this flow. The present study attempts to move beyond the current state of analysis by numerically examining the details of the flow on a microscopic scale. In a process such as the combustion of Ti and C, the fluid intermediate, molten Ti, arises from the highly exothermic and rapid nature of the reaction. The molten components then spread by capillary action, surface tension driven convection, and surface wetting. The spreading action is essential to the success of the process since the reaction cannot proceed to any great extent until an interface is established between the components. The effects we wish to resolve here are the alterations of the pressure gradients experienced in the capillary spreading due to the other flow mechanisms and to the finite, curved character of the fluid reservoir. Experimental observation of such effects appear to be exceedingly difficult. On the other hand, readily available simulations may give us some qualitative insight into the flow character of condensed phase combustion synthesis and so we have decided to proceed along these lines.

THE COMBUSTION SYNTHESIS OF Ti + C

The combustion process

In condensed phase combustion synthesis, one typically begins with powders of the elements, mixes them uniformally, and then cold presses them into a desired shape. The green body is then thermally heated by a resistively heated strip or wire filament. Once the reaction is initiated the exothermic reaction generates the addition heat required to complete the process.

If the sample is heated locally, a combustion wave may develop and propagate throughout the rest of the sample. Ordinarily the peak temperatures in the combustion wave are sufficient to melt one or more of the components of the system. There is considerable evidence for the melting of Ti in the Ti + C reaction [4-7]. Also we will be concerned with the case where a combustion wave is supported.

Combustion rates

For the Ti + C system, propagation rates of 0.5 to 3.0 cm/s are observed depending on the initial temperature and particle sizes. The later is of particular interest here and has been explored by Okolovich et al. [8] and by Nekrasov et al. [9]. Their general findings with respect to the size of the metallic component are summarized in Fig. 1. The results are interpreted in terms of capillary spreading rates. When the metal particles are small, the spreading takes place quickly relative to the time of the reaction. In this case the rate of combustion wave propagation is limited by the characteristic time of reaction. When the metal particles are large, >0.1 μm, the spreading time is long relative to the time of reaction. In this case the rate of propagation is limited by the characteristic spreading which is thought to exceed the time required for capillary pore blockage by product. Qualitatively this picture is probably correct. As we shall see however there are many more flow mechanisms than just capillary flow.

WETTING AND SPREADING DYNAMICS IN POWDER SYSTEMS

Numerical fluid flow code: SOLAVOF

In order to step beyond the simple picture given above, we employ numerical simulation methods provided through the SOLAVOF hydrocode [10]. The attractive features of the code include free surface tracking, surface tension effects, wall contact effects, and obstacle configurations. The code deals only with the Navier-Stokes equation, the focus of this study, and ignores heat flow and reactivity. The fluid is tracked by a "volume-of-fluid" method [11] which identifies free surfaces as fluid bearing mesh cells with void cells adjacent to them. A separate fluid configuration function evolves with its own equation of motion to follow the development of the free surface.

Cylindrical fluid configurations

A series of simulations with differing void volumes for a fixed fluid volume is performed to understand the influence of void space in the rate and final configuration of the fluid. The initial configuration of the fluid is a cylinder 20 μm in height and 20 μm in diameter (Fig. 2a). In the case shown here, the fluid to void ratio is 3.02. In addition, for each void volume value considered, a simulation is run for both the zero gravity and the one earth gravity cases. As shown in Fig. 2b, when no gravitational force is applied, the configuration evolves into two rings of void after 8.8 μs. On the other hand, when a gravitational force is applied downward,

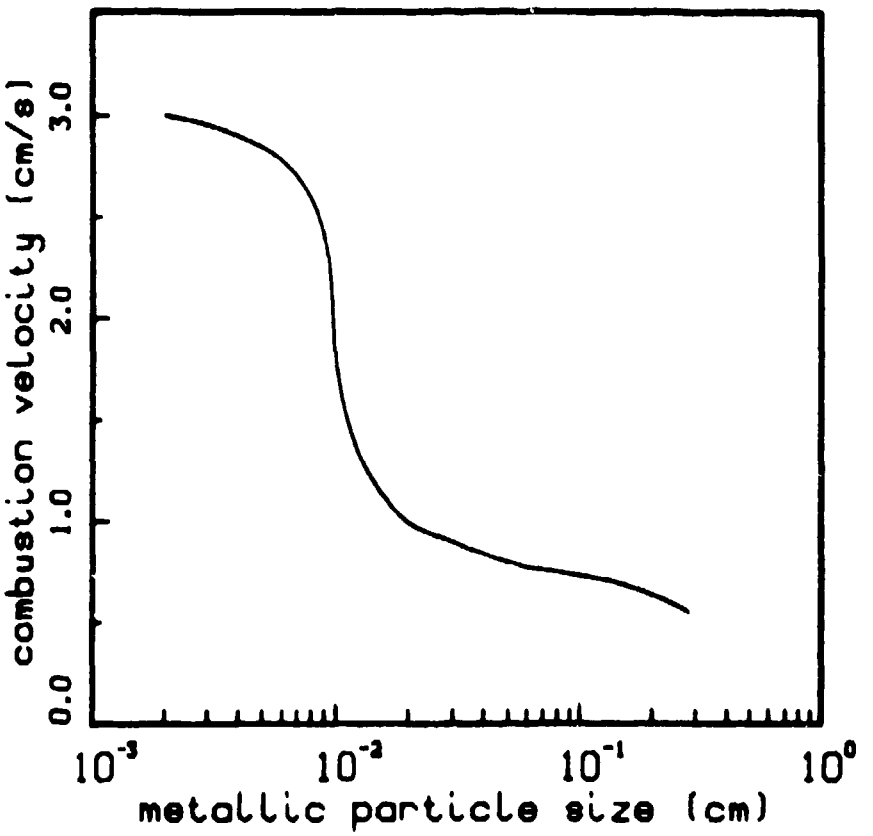

Figure 1. Dependence of Ti + C combustion velocity on metal particle size. From Ref. 9.

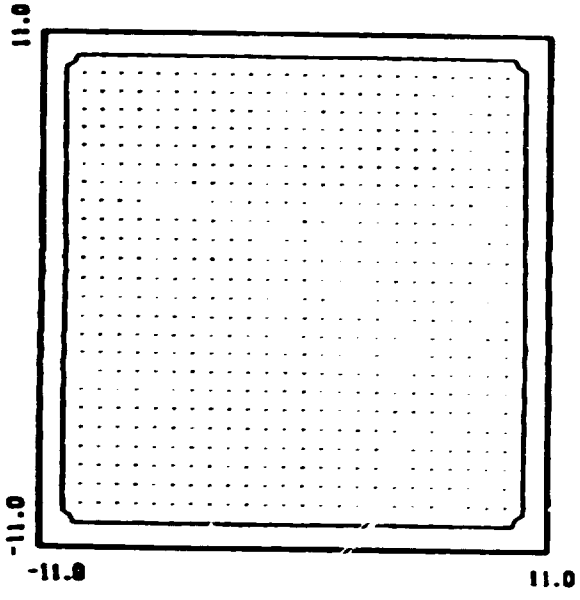

Figure 2a. Initial cylindrical configuration with r=10 μm and h=20 μm. Approximate theoretical density is 0.86.

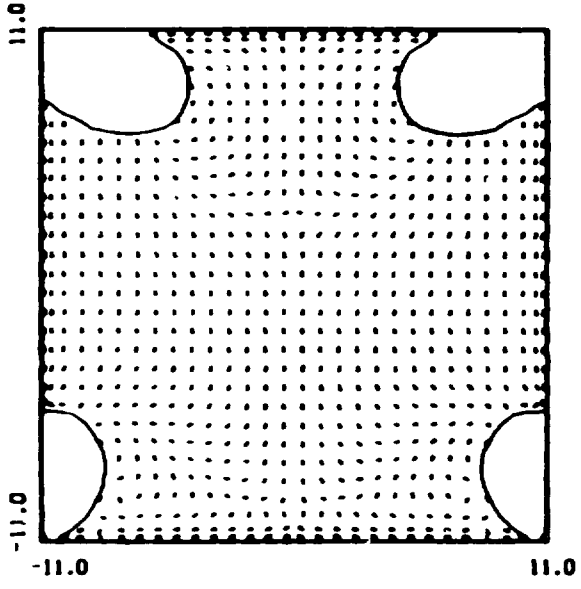

Figure 2b. Fluid configuration after 8.8 μs with no gravity. Upper void ring appears to be growing still.

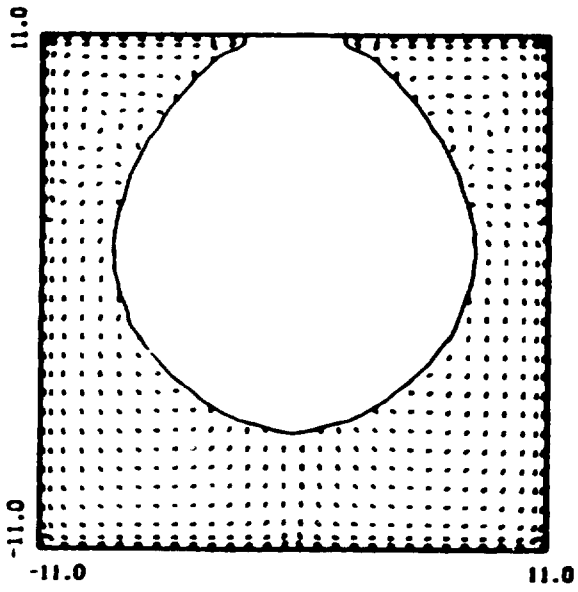

Figure 2c. Fluid configuration after 8.8 μs with gravity. Void rings appear to have coalesced into a single spherical void.

the lower ring collapses and the upper one expands into a single spherical void (Fig. 2c). However this phenomena is not observed in the other systems and the final configurations are very similar for the gravitational and nongravitational cases.

To explore this situation further, two bubbles are placed one above another as shown in Fig. 3a and are allowed to evolve. If the simulation were perfect with no gravitational force, the system would be steady. But as is evident in Fig. 3b the lower bubble expands at the expense of the upper one. Also evident are the flow fields causing the collapse. On the other hand, with a gravitational force present the upper void expands (Fig. 3c) as expected on the basis of Fig. 2c. In retrospect we see in Fig. 2b that the upper void is actually growing but has not evolved to the extent of Fig. 2c. Apparently the two bubble configuration is only metastable and is quite susceptible to upset by small numerical or physical perturbations. Also necessary for this peculiar phenomena is the closed volume of the whole system. An open system is not expected to behave in this fashion. Nevertheless, the calculations suggest that gravitational or other destabilizing forces such as surface tension or wetting may lead to void coalescence in a nonbouyant mode.

WETTING AND CAPILLARY DYNAMICS

To assess the influence of spreading motion, spheroidal fluid configurations are placed in contact with a 0.1 μm capillary (Fig. 4a). The rise in a 0.1 μm capillary with the parameters set to those for Ti and C has a profile which becomes parallel to the Poiseuille model [8, 9, 12] after two times the viscous dissipation time (Fig. 4b). By comparison when the spheroidal reservoir is allowed to evolve under surface tension and contact forces the profiles appear to evolve more quickly as shown in Fig.-4C. The outcome may depend on the vertical-to-horizontal aspect ratio. That is, if the metal droplet is elongated vertically, the fluid may pull away from the wall thereby depriving the capillary of a fluid reservoir. One should also note that the spreading times for the 10 μm particles is much longer than the viscous dissipation time of the 0.1 μm capillary. This appears to contradict a key assumption in the analyses on Ref. 8 and 9.

CONCLUSION

Gravitational forces can affect bubble coalescence by nonbouyant means under the proper conditions, although the conditions are expected to be rare in combustion synthesis. Finite curved reservoirs can drive capillary flow at microscopic dimensions due to surface tension and wall contact forces which cause the void and the metal to be completely reconfigured in a combustion synthesis of TiC from powders of its elements.

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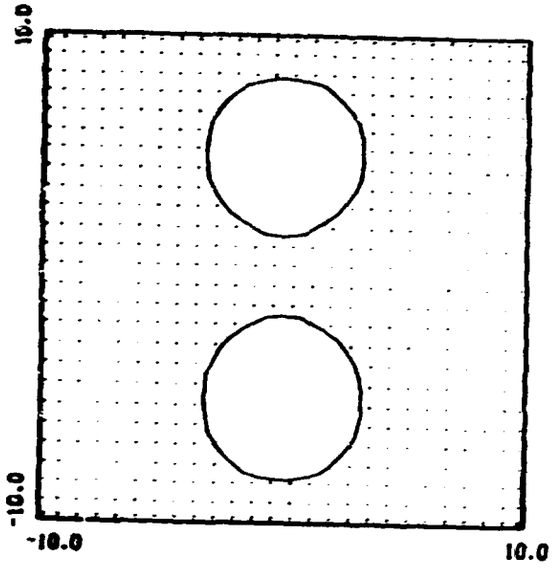

Figure 3a. Initial metstable two bubble configuration. Each bubble fluid is quiescent. into a single spherical void.

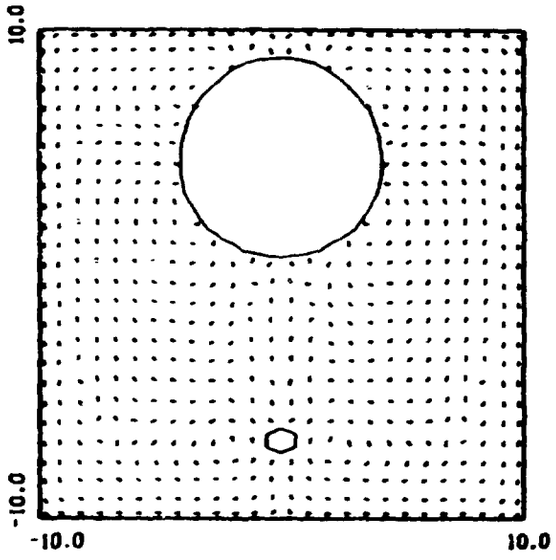

Figure 3b. Flow field after 5.9 μs with gravity shows the upper bubble expanding and the lower bubble contracting.

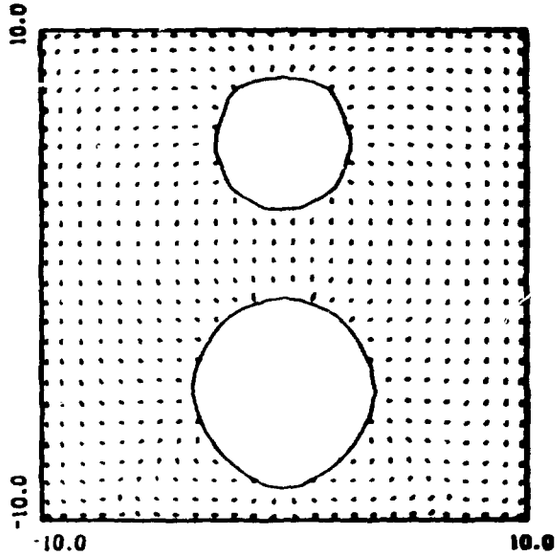

Figure 3c. Flow field after 5.9 μs with no gravity shows opposite process, upper bubble contracting and lower bubble expanding.

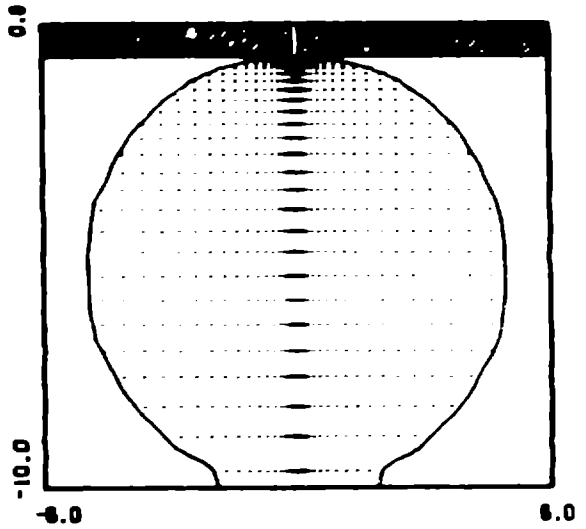

Figure 4a. Initial configuration of 10 μm diameter droplet in contact with 0.1 μm capillary.

Figure 4b. Rise in 0.1 μm capillary after 23 ns from a quiescent reservoir simulated by a continuative boundary.

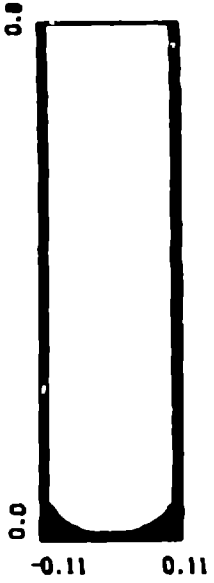

Figure 4c. Rise in 0.1 μm capillary after just 1.2 ns from a 10 μm reservoir under going wall-driven convection.

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